Supporting Information

Ladder- and bridge-like polynorbornenes with phosphate linkers: facile one-pot synthesis and excellent properties

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Experimental Part

**Synthesis of 1,4-Bis(10-Undecylcarbonyloxy)-cis-2-Butene (TA)**

cis-1,4-Butenediol (1.76 g, 20.0 mmol), undecenoic acid (8.83 g, 48.0 mmol), DMAP (0.60 g, 4.8 mmol), CH₂Cl₂ (65 mL), and THF (15 mL) were charged into a 250 mL round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere, and the mixture was stirred at 0 ºC for 15 min. EDCI (9.21 g, 48 mmol) was then added to the former solution, and stirred for 3 days after the solution warmed to room temperature. The resulting solution was washed three times with deionized water (3 × 80 mL), and the organic layer was dried over anhydrous Na₂SO₄. Solvent was then evaporated and the crude product was purified by silica gel chromatography eluted with CH₂Cl₂ to give a clear colorless liquid (6.12 g, 72.8% yield). ¹H NMR (CDCl₃): δ (ppm) 5.82–5.73 (m, 4H, CH=CH + CH₂=CH), 5.02–4.96 (m, 4H, CH₂=CH), 4.72 (s, 4H, OOC=CH₂CH=CH), 2.27–2.18 (d, 4H, CH₂CH₂OCO), 2.06–1.92 (d, 4H, CH₂=CHCH₃), 1.69–1.53 (d, 4H, CH₂CH₂OCO), 1.41–1.05 (m, 20H, CH₂(CH₂)₅CH₂).


**Synthesis of N-2-Hydroxyl-Ethyl-Norbornene-Dicarboximide (Compound 1)**

5-Norbornene-2,3-dicarboxylic anhydride (9.84 g, 60 mmol) and 80 mL of CH₃OH were charged into a 250 mL Schlenk flask. A solution of ethanolamine (3.66 g, 60 mmol) in CH₃OH (20 mL) was then added dropwise to the former solution at 0 ºC. The reaction mixture was allowed to warm to room temperature and stirred at 65 ºC for 24 h. Removal of the solvent and further purified through recrystallization to afford a white crystal with a yield of 76.8% through recrystallization from ethanol. ¹H
NMR (CDCl$_3$): $\delta$ (ppm) 6.32–6.26 (s, 2H, $CH=CH$), 3.86–3.72 (m, 4H, NCH$_2$CH$_3$OH), 3.61–3.52 (m, 2H, CHCON), 3.43–3.25 (m, 2H, CHCH$_2$CH), 1.81–1.75 and 1.64–1.49 (d, 2H, CHCH$_2$CH). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 178.6, 138.5, 62.3, 46.1, 43.5, 37.5, 33.6. LC: single peak was observed. EI/MS: Calcd. for C$_{11}$H$_{13}$O$_3$N: 207.19; Found: 207.17. Anal. Calcd for C: 63.77, H: 6.28, O: 23.19; Found C: 63.79, H: 6.27, O: 23.19.

**Synthesis of N-2-Carboxyl-Ethyl-Norbornene-Dicarboximide (Compound 2)**

5-Norbornene-2,3-dicarboxylic anhydride (6.56 g, 40 mmol) and 60 mL of CH$_3$OH were charged into a 250 mL Schlenk flask. A solution of 3-aminopropanoic acid (3.56 g, 40 mmol) in CH$_3$OH (10 mL) was then added dropwise to the former solution at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred at 65 °C for 24 h. The resulting solution was filtered off and the filtrate was washed three times with deionized water (3 × 80 mL), and the organic layer was dried over anhydrous Na$_2$SO$_4$. Solvent was then evaporated and the crude product was purified by vacuum distillation to give a yellowish viscous liquid with a yield of 82.5%. $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 6.28–6.23 (s, 2H, $CH=CH$), 3.79–3.64 (m, 4H, NCH$_2$CH$_3$COOH + CHCON), 3.27–3.22 (m, 2H, CHCH$_2$CH), 2.51–2.47 (m, 2H, CH$_2$OCOCH$_2$), 1.61–1.55 and 1.50–1.47 (m, 2H, CHCH$_2$CH). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 176.2, 175.1, 137.5, 43.9, 37.3, 36.8, 35.0, 33.6. GC: single peak was observed. EI/MS: Calcd. for C$_{12}$H$_{13}$O$_4$N: 235.2375; Found: 235.2369. Anal. Calcd for C: 61.27, H: 5.57, O: 27.20; Found C: 61.26, H: 5.57, O: 27.19.
Fig. S1  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for terminating agent.
Fig. S2  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for compound 1.
Fig. S3  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for compound 2.
Fig. S4  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for M1a.
Fig. S5  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for M1b.
Fig. S6  ATR–IR spectra for (a) M1a and (b) M1b.
Fig. S7  MALLS–GPC traces for ladder-like (a) poly(1a) ([M]: [C] = 10: 1–30: 1) and (b) poly(1b) ([M]: [C] = 10: 1 or 30: 1) prepared using C3 as catalyst at 30 °C.
Fig. S8  MALLS–GPC traces for ladder-like poly(1a) prepared in different reaction conditions (a) C1 as catalyst at 30 or 50 °C and (b) C2 as catalyst at 30 °C.
Fig. S9  $^{13}$C NMR spectra for (a) double-stranded poly(1a), (b) telechelic double-stranded poly(2a), and (c) bridge-like poly(3a).
Fig. S10  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for double-stranded poly(1b).
Fig. S11  MALLS–GPC traces for ladder-like poly(2b) and bridge-like poly(3b).
Fig. S12  (a) $^1$H NMR and (b) $^{13}$C NMR spectra for telechelic double-stranded poly(2b).
Fig. S13 (a) $^1$H NMR and (b) $^{13}$C NMR spectra for bridge-like poly(3b).